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(21) International Application Number: PCT/IB97/01329 (22) International Filing Date: 23 October 1997 (23.10.97) (30) Priority Data: B096A000536 24 October 1996 (24.10.96) IT (71) Applicant (for all designated States except US): I.N.P. - INDUSTRIAL NATURAL PRODUCTS S.R.L. [IT/IT]; Via San Vittore, 47, I-20123 Milano (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): PIFFERI, Piergiorgio [IT/IT]; Via Ortolani, 3, I-40100 Bologna (IT). SPAGNA, Giovanni [IT/IT]; Via Cavour C., 233, I-97019 Vittoria (IT). MANENTI, Italo [IT/IT]; Via G. di Vittorio, 13, I-40068 S. Lazzaro di Savena (IT). (74) Agent: DALL'OLIO, Giancarlo; Interbrevetti S.r.l., Via del Cestello, 13, I-40124 Bologna (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR REMOVING PESTICIDES AND/OR PHYTODRUGS FROM LIQUIDS USING CELLULOSE, CHITOSAN AND PECTOLIGNINCELLULOSIC MATERIAL DERIVATIVES (57) Abstract <p>The method for removing pesticides and/or phytodrugs from alimentary liquids, from drinkable and superficial waters and from waste waters includes that such liquids are treated with chitin, or with alkyl and aryl derivative of cellulose, of hemicellulose, of chitin, of chitosan, of pectin and of pectolignin-cellulosic materials. After treatment with such powdery adsorbents for a time period until 24 hours at a concentration ranging between 10 and 4000 grams for hectoliter of treated liquid, and at temperatures up to 60 °C, the adsorbent is separated from the liquid getting the removal of the phytodrugs and/or pesticide up to 100 % of their initial value.</p>		

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METHOD FOR REMOVING PESTICIDES AND/OR PHYTODRUGS
FROM LIQUIDS USING CELLULOSE, CHITOSAN AND
PECTOLIGNINCELLULOSIC MATERIAL DERIVATIVES

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TECHNICAL FIELD

The present invention relates to liquid
treatment with materials suitable to extract noxious
10 substances therefrom.

Particularly the invention relates to a
treatment method of alimentary liquids, such as oil,
wine, must, fruit juices, alcoholic or
hydroalcoholic extracts, drinkable waters or waters
15 to be made drinkable, irrigation waters with
fertilizer or industrial waste waters, in order to
reduce drastically the content of pesticides or
phytodrugs.

20

BACKGROUND ART

In fact, the pesticide and/or phytodrug
content inside essentially alimentary products can
25 result extremely dangerous for the consumer health
depending on the assumption frequency and the
contamination level of the products, particularly
alimentary liquids.

Therefore the presence of phytodrugs and/or
30 pesticides must be reduced to a minimum values, in
order to reduce the risks for public health but also
to promote the image and the quality of the
alimentary liquid, of drinkable or to be made
drinkable or waste water.

35 The commonly used adsorbent for filtering the

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alimentary and non-alimentary liquids are based on bentonite, silicates, resins and coal. The bentonite and the silicates are often used for removing pesticides and/or phytodrugs, although the removal
5 rate is poor, and however not exceeding 30%.

Such adsorbents, for instance the active charcoal, have further drawbacks such as the lack of selectivity and an elevated cost, reducing drastically the industrial application thereof.

10

DISCLOSURE OF THE INVENTION

The main object of the invention is to
15 propose a method for treating alimentary and not alimentary liquids, particularly musts, wines, vegetable or fleshy or clear citrus juices, drinking waters or waters to make drinkable, river and waste waters, vegetable food oils, such that, after the
20 treatment, the pesticide and/or phytodrug content in that liquids is substantially reduced and, at the same time, widely improving hygienic and organoleptic quality thereof.

Another object of the invention is to propose
25 a substance able to remove selectively the phytodrugs and/or the pesticides from the treated liquids and to be moreover recyclable for following uses.

Further object of the invention is to propose
30 a simple realization and an economically advantageous method.

The above mentioned objects are achieved in accordance with the content of the claims.

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BEST MODE OF CARRYING OUT THE INVENTION

The method according to the invention is used to remove totally or at least partially the pesticides and/or phytodrugs from alimentary and not liquids by mixing thereto a powdery or granular adsorbent material including chitin, or alkylesters or arylesters of cellulose, of hemicellulose, of chitin, of chitosan, of pectin or of pectolignincellulosic materials obtained as by-products in agro-industry processes, or of their mixtures.

The liquids to be treated are firstly put to a temperature ranging between 4°C and 60°C, then a variable amount of adsorbent material, ranging from 10 to 4000 grams for hectoliter of liquid to be treated, is mixed thereto.

The so obtained mixture is stirred for a period ranging from 0,1 to 24 hours, then it is filtered for removing the adsorbent material from the alimentary and non-alimentary liquid when the pesticides and/or phytodrugs therein have been captured, usually almost entirely, by the adsorbent material itself.

The alimentary liquids are essentially constituted by grape must, wine, beer, fruit or citrus juices, aqueous or hydroalcoholic extracts or fruit, citrus or horticultural concentrates, vegetable oil.

Advantageously the above mentioned liquids are firstly centrifuged for removing the material in suspension so obtaining a relatively clear liquid.

The non-alimentary liquids essentially include drinkable or to be made drinkable waters, irrigation waters with fertilizer or industrial

polluted waters.

The alimentary or non-alimentary liquids are heated for facilitating the pesticide and/or phytodrug kinetic of adsorption by means of
5 adsorbents.

The adsorbent material includes mainly the chitin, the chitosan, chitin, cellulose, hemicellulose derivatives or derivatives of pectolignin-cellulosic structures such as citrus
10 peels, apple residues, grape skins, sugar beet ribbons, or diethylaminoethylcellulose derivatives (DEAE-cellulose). These derivatives are respectively alkylesters and arylesters in which the R-CO group is of the acid C₂, C₄, C₆, C₈, C₁₀, C₁₂, C₁₈ and the
15 aryl group is the residue of the acids benzoic, paramethylbenzoic, paramethoxybenzoic, 4-hydroxybenzoic, 3-4-dihydroxybenzoic, phenylacetic, caffeic, cinnamic, hydroxycinnamic, vanillic, ferulic, syringic, ortho and paracoumaric,
20 anisic, or the benzyl-group and in which the substitution degree of the alcoholic group with acid residue ranging from 1 to 3.

The percentage of the alkyl or arylester derivate of the chitin, chitosan, cellulose, hemicellulose, diethylaminoethylcellulose (DEAE -
25 cellulose), has a substitution degree of the alcoholic group ranging between 1 and 3.

The adsorbent is obtained as the ester powder and has a particle size less than 3 mm., preferably
30 of 0,25 mm.

The temperature the alimentary and non alimentary liquids are carried during the mixing phase with the powdery or granular substance ranges from 1°C to 60°C relative to the liquid to be
35 treated. That is to say if the liquid is beer the

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optimal temperature is 20°C, while if it is vegetable oil the optimal temperature is 15°C, and finally if it is waste waters the temperature can reach and also exceed 60°C. In fact it is
5 ascertained that, relatively to the chemical-physic characteristics of different liquid to be treated, it can be reached temperatures next to the freezing or boiling temperatures of the liquids.

The concentration of powdered or granular
10 adsorbent in the alimentary or non liquid ranges between 10 and 4000 grams for hectoliter of liquid and varies relating to the following parameters:

- it is as much greater as greater is the quantity of pesticide or phytodrug dissolved in the liquid to
15 be treated;
- it is as much greater as smaller is the time within which it is wished to remove the pesticide or phytodrug elements from the alimentary or not liquid;
- 20 - it is as much smaller as greater is the temperature to which the liquid to be treated can be brought without altering the organoleptic characteristics;
- it depends on the viscosity degree of the liquid
25 to be treated and it is as much greater as more the liquid is viscous.

Anyway, it is noted that satisfactory results of considerable pesticides or phytodrugs removal are achieved with an optimal concentration of 1500 grams
30 for hectoliter of liquid to be treated which is led to a temperature of 25°C and mixed with adsorbent for 3 hour time.

The powdery or granular adsorbent material, after being mixed with the liquid to be treated is
35 separated therefrom by centrifugation or by

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precipitation through settling of the mixture depending on the liquid to be treated and on the time in which it is wished to remove the pesticides or phytodrugs from the liquid.

- 5 Further particularities will be clear from the description of some preferred examples of practical carrying out of the method according to the invention.

10 EXAMPLE 1

A liter of wine, for instance Trebbiano, containing 1 parts per million (ppm) of Penconazole (from the Pesticide Manual - ninth edition - 1993, n.9375) and of Vinclozolin (from the Pesticide
15 Manual - ninth edition - 1993, n.12300), is added with 5 grams/liter of benzoilcellulose with 1,8 substitution grade.

After 3 hours of stirring at the temperature of 20°C it is filtered, with a filter of glass
20 septum, and the residue of the pesticide is determined with the liquid chromatography. It is noted a Penconazole and Vinclozolin decrease of 70% and 90% respectively.

25 EXAMPLE 2

A clear apple juice, obtained by pressing with band press of the crushed GOLDEN apples after treatment with pectinase enzyme at a temperature of 45°C for 90 minutes, is added with diatomeous earth
30 in the proportion of 15 grams/liter and therefore centrifuged.

This centrifuged mixture, containing 1,5 ppm of Procymidone (from the Pesticide Manual - ninth edition - 1993, n. 10020), is added with 1% of
35 octanoilchitin powder having diameter granules of

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0,25 mm., and is maintained for 2 hours at the temperature of 25°C, in a non-oxidant atmosphere. After such time, it is filtered and analysed by HPLC measuring a 86% decrease of Procymidone in the same
5 filtrate.

EXAMPLE 3

A 2 liter sample of river water, in the example picked up from Po river near Ferrara city,
10 is added with 3 ppm. of Iprodione (from the Pesticide Manual - ninth edition - 1993, n.7330). It is added 38 grams/liter of benzoilcellulose powder with granules having diameter smaller than 2,5 mm. and the mixture is stirred for 12 hours at the
15 temperature of 50°C. After filtration, the residual content of Iprodione in the water is determined by chromatography HPLC, which is 0,20 ppm.

EXAMPLE 4

20 A waste water sample of agro-industrial origin contains 1,5 ppm of Fenarimol (from the Pesticide Manual - ninth edition - 1993, n.6030), 1,0 ppm of Triadimenol (from the Pesticide Manual - ninth edition - 1993, n.11830) and 1,3 ppm of
25 Penconazole. After centrifugation in presence of diatomeous earth at 1,5 grams/liter concentration and having 0,20 mm. diameter granules, 25 grams/liter of diethylaminoethylcellulose benzoilderivative, of 1 substitution degree and as
30 powder of 0,25 mm. diameter granules, are added to the centrifugate mixture. The mixture is stirred for 2 hours at the temperature of 20°C, then is centrifuged and the water pesticide content is analysed by HPLC chromatography.

35 A 90% removal of Fenarimol, 55% of

Triadimenol and 84% of Penconazole is measured.

EXAMPLE 5

5 A fleshy citrus juice containing 2 ppm of Benalaxyl (from the Pesticide Manual - ninth edition - 1993, n. 660), is centrifuged for 15 minutes at 3000 revolutions/minute at the temperature of 4°C. A juice with a 95% cloudiness decrease is obtained. The obtained centrifuged mixture is therefore added
10 with 10 grams/liter of powdery benzoilchitin, having 1,8 substitution degree, diameter granules ranging between 0,125 mm. and 0,250 mm. and at the temperature of 20°C for 60 minutes, by stirring in nitrogen atmosphere. After this time it is
15 centrifuged at 3000 revolutions/minute for 15 minutes at the temperature of 4°C. The analysis of the juice by means of HPLC chromatography reveals a decrease of 85% of pesticide.

20 EXAMPLE 6

A liter of red wine contains 1 ppm of each of the pesticides Fenarimol, Procymidone, Penconazole, Iprodione. It is added 15 grams/liter of powdery cellulose triacetate, with 0,25 mm. granules, by
25 stirring at 20°C temperature for four hours in nitrogen atmosphere. It is then filtered and, after chromatographic analysis, a percentage decrease of pesticides is measured respectively of 53%, 65%, 75% and 68%.

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EXAMPLE 7

A white grape must, obtained by mild pressing with VASLIN press, is centrifuged and added with 1,5 ppm of Penconazole, Iprodione and Benalaxyl. It is
35 added 10 grams/liter of benzoilchitosan and 10

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grams/liter of hexylchitosan, as powder of particle size ranging between 0,1 and 0,25 mm. It is stirred for 120 minutes at the temperature of 20°C and then it is centrifugated. The analysis of that
5 centrifuged, by HPLC chromatography, reveals a decrease of respectively 65%, 59% and 83% of the single above-mentioned pesticides.

EXAMPLE 8

10 A sample of 1 liter ALBANA wine, containing 1 ppm. of each of pesticides Iprodione, Procymidone, Penconazole, is treated with the benzoil derivative of apple residue obtained by pressing the juice with band press. Such residue, boiled for 5 minutes to
15 remove the soluble substances such as sugars, phenols and acids with water in the ratio 1:5, is then filtered and suspended in water until the complete absence of such substances, which are tested with FOLINCIOCALTEU reagent. Therefore it is
20 dried at a temperature of 65°C in oven and treated with benzoil chloride in pyridine according to the typical methods of the organic chemistry at a temperature of 50°C to get the benzoilderivative of pectins, cellulose, hemicellulose, contained in the
25 residue with a OH substitution degree ranging from 1 to 2,8. Such derivative is added to wine in quantity of 40 grams/liter. After 180 minutes of stirring at the temperature of 25°C, the mixture is filtered and the analysis of filtered wine reveals a decrease of
30 pesticides greater than 80%.

EXAMPLE 9

A sample of 0,5 olive oil litres containing 1,5 ppm. of Procymidone and Triadimenol, is added
35 with 10 grams of a mixture of benzoilchitosan and

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benzoilchitin, at a temperature of 20°C, and stirred in the dark for 60 minutes, in N₂ atmosphere. After such time it is filtered on a glass porous septum, and the residual quantity of the pesticides is
5 analysed by HPLC chromatography at 210 nm. The analysis reveals a decrease of 86% for Procymidone and of 79% for Triadimenol.

The principal advantage of the invention is
10 to provide a method for treating alimentary and not-alimentary liquids, particularly musts, wines, vegetable or pulpy or clear citrus juices, drinking waters or waters to be made drinkable, river waters and waste waters, vegetable food oils, so that,
15 after the treatment, the content of pesticides and/or phytodrugs in that liquids is almost eliminated and that, at the same time, it is improved their hygienic quality and organoleptic properties.

20 Another advantage of the invention is to provide a substance suitable to remove selectively the phytodrugs and/or the pesticides from the treated liquids, from which it is firstly added and then separated, and it is also a recyclable
25 substance for subsequent uses.

Further advantage is to provide a simple realization and economically advantageous method.

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CLAIMS

1) Method for removing pesticides and/or
phytodrugs from alimentary and non-alimentary
5 liquids characterized in that each of said liquids,
is carried to a temperature ranging between 1°C and
60°C, is added with a powdery or granular adsorbent
material essentially constituted by chitin or
alkylesters or arylesters of cellulose,
10 hemicellulose, chitin, chitosan, pectin, or
pectolignincellulosic materials, or mixtures
thereof, in such a quantity that in a hectolitre of
liquid is contained an amount from 10 to 4000 grams
of said adsorbent, the mixture so obtained being
15 stirred for a time period ranging from 0,1 hours to
24 hours, and therefore filtered for removing the
powdery or granular substance which has removed the
cited pesticides and/or phytodrugs.

2) Method according to claim 1, characterized
20 in that said alimentary liquids essentially include
grape must, wine, beer, fruit or citrus juices,
aqueous or hydroalcoholic extracts or fruit, citrus
horticultural concentrates, vegetable oil.

3) Method according to claim 1, characterized
25 in that said non-alimentary liquids essentially
include drinking waters or waters to be made
drinkable, irrigation waters with fertilizer or
industrial waste waters.

4) Method according to claim 1, characterized
30 in that said powdery or granular material has got a
diameter granules not exceeding 3 mm.

5) Method according to claim 1, characterized
in that said adsorbent material includes the esters
containing the acid residue of acid that can be C₂,
35 C₄, C₆, C₈, C₁₀, C₁₂, C₁₈ and in which the

substitution degree of the alcoholic group with the acid residue ranges from 1 to 3.

6) Method according to claim 1, characterized in that said adsorbent material includes esters in which the acid residue is the acid benzoic, or paramethoxybenzoic, or paramethylbenzoic, or 4-hydroxybenzoic, or 3-4-dihydroxybenzoic, or phenylacetic, or caffeic, or cinnamic, or hydroxycinnamic, or vanillic, or ferulic, or syringic, or ortho and paracoumaric, or anisic, or the benzyl group with the substitution degree of the alcoholic group ranging between 1 and 3.

7) Method according to claim 1, characterized in that said powdery or granular material is obtained from citrus peels.

8) Method according to claim 1, characterized in that said powdery or granular material is obtained from pressed apple residue.

9) Method according to claim 1, characterized in that said powdery or granular material is obtained from grape skins.

10) Method according to claim 1, characterized in that said powdery or granular material is obtained from exhausted sugar beet ribbons.

11) Method according to claim 1, characterized in that said powdery or granular material is obtained from pectins.

12) Method according to claim 1, characterized in that said powdery or granular material is obtained from chitin.

13) Method according to claim 1, characterized in that said powdery or granular material is obtained from chitosan.

14) Method according to claim 1,

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characterized in that said powdery or granular material is obtained from diethylaminoethylcellulose.

- 15 15) Chitin, alkylester or arylester of cellulose, of hemicellulose, of chitin, of chitosan, of pectin or of pectolignincellulosic materials used as adsorbents of pesticides and/or phytodrugs from alimentary or non-alimentary liquids.

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INTERNATIONAL SEARCH REPORT

In. ational Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J20/24 B01D15/00 C12H1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J B01D C12H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 25437 A (ABION BETEILIGUNGS-UND VERWALTUNGSGES.) 22 August 1996 see page 10, paragraph 2 see page 20-22; claims 1,18 ---	1, 12, 13, 15
Y	EP 0 501 381 A (PIFFERI) 2 September 1992 see page 5; claim 1 ---	1, 12, 13, 15
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A	DE 41 29 874 C (SÄCHSISCHE PHARMAWERK WEINBÖHLA) 24 September 1992 -----	

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☒ Patent family members are listed in annex.

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Information on patent family members

International Application No

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